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**REACTIONS OF XENON WITH
CERTAIN STRONG OXIDIZING
AGENTS**

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REACTIONS OF XENON WITH CERTAIN STRONG OXIDIZING AGENTS

By Gary L. Gard, Francis B. Dudley and George H. Cady

The syntheses of the xenon fluorides^{1,2,3} and xenon hexafluoro- (platinate⁴, rhodate⁵, and ruthenate⁶) suggested that other strong oxidizing agents could possibly react with xenon. Therefore, the reactions of xenon with trifluoromethyl hypofluorite (CF_3OF), oxygen difluoride (OF_2), fluorine fluorosulfate (FOSF) and peroxydisulfuryl difluoride ($\text{F}_2\text{O}_2\text{OSF}_2$) were studied. One set of reactions was carried out in a prefluorinated 1.5 liter nickel vessel. The experimental conditions and results are tabulated below:

Reactants $\text{Y} + \text{Xe}$	Molar Ratio $\text{Y}:\text{Xe}$	Minimum Temp. ($^{\circ}\text{K}$) for Reaction	Maximum Temp. ($^{\circ}\text{K}$) Attained	Products
$\text{F}_2\text{O}_2\text{OSF}_2 + \text{Xe}$	3:1	---	750	$\text{Xe} + \text{O}_2 + \text{SO}_2\text{F}_2$
$\text{OF}_2 + \text{Xe}$	1:1	560	660	?

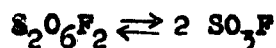
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$S_2O_6F_2 + Xe$

The mixture of $S_2O_6F_2$ and Xe had a total pressure of 160 mm at 300°K. As the mixture was heated the pressure increased ideally in proportion to the absolute temperature up to about 500°K. Above this temperature the rate of increase in pressure was abnormally great because of the dissociation of $S_2O_6F_2$ into free radicals⁷ according to

7. F.B. Dudley and G.H. Cady - in press.

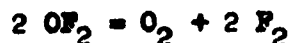
the equation:



The observed abnormality was that expected for this equilibrium. If xenon fluorosulfate had been formed, the total pressure would have been smaller than that observed. There was no evidence for a reaction involving xenon.

$OF_2 + Xe$

When the temperature of an equimolar mixture of oxygen difluoride and xenon having a total pressure of 104.5 mm at 452°K was slowly raised, the pressure increased ideally with the absolute temperature up to about 560°K. Above this temperature the pressure decreased, indicating that chemical combination was in progress. The product of the reaction was not studied. It is probably significant that decomposition of oxygen difluoride by the reaction



occurs at temperatures above about 530°K. A pressure vs. rising temperature curve for a sample of oxygen difluoride shows an abnormal increase in pressure above 530°K because of this dissociation. When

xenon was present the reaction of F_2 with Xe probably balanced the dissociation of OF_2 to permit the number of molecules in the gas to remain about constant from 530° to $560^\circ K$. Above this temperature a decrease in the number of molecules occurred. It appears likely that xenon did not react directly with OF_2 but did react with F_2 formed from oxygen difluoride, as the pressure vs. temperature curves for mixtures of xenon and fluorine showed that chemical combination occurred at temperatures as low as $390^\circ K$.

Another set of reactions was carried out in prefluorinated monel pressure tubes equipped with Hoke needle valves and brass $10/30$ connections. The experimental conditions and results are tabulated below:

Reactants y + xe	Molar Ratio y:xe	Pressure (atms.) and Temp. ($^\circ K$)		Products
		P	T	
$CF_3OF + Xe$	2.2:1	about 250	500	XeF_2 and CF_3OOCF_3
$FSO_2F + Xe$	2.2:1	about 150	450	XeF_2 and $S_2O_6F_2$

The above pressures were estimated from the amounts of materials present and from the temperature and volume of the system.



0.0280 mole of CF_3OF was distilled into a prefluorinated Monel tube (volume 6 cc). To this was added 0.0125 mole of xenon. The tube was put into a heated oven and kept at a temperature between 220 and $250^\circ C$ for seven days. (CF_3OF decomposes reversibly into COF_2 and fluorine at temperatures greater than about $275^\circ C$.) The tube was then withdrawn from the oven and cooled quickly in a water bath. The tube was further cooled to $-78^\circ C$ and the volatile product was pumped away

through a trap held at liquid nitrogen temperature. The volatile materials other than Xe were shown to be CF_3OF and CF_3OOCF_3 by infra-red identification. The material remaining in the tube was shown by chemical analysis to be xenon difluoride. Analyses gave the following results:

	<u>Expt'l</u>	<u>Theor.</u>
Xenon %	76.3 76.5	77.6
F %	21.98	22.4

The mechanism of this reaction may have involved the dissociation of a molecule of CF_3OF into a fluorine atom and a $\text{CF}_3\text{O}\cdot$ free radical. The fluorine would have been available to combine with xenon and free radicals could have combined to form CF_3OOCF_3 .



0.0079 mole of FSO_3F was distilled into a prefluorinated Monel tube (vol. 3 cc) 0.0037 mole of xenon was added to this. The tube was placed in a heated oven and kept for four days at a temperature between 170 and 180°C. (FSO_3F decomposes at temperatures greater than 200°C.) The tube was then withdrawn from the oven and cooled quickly in a water bath. The tube was cooled to -14°C and the volatile product was pumped away through a trap held at liquid- O_2 temperature. The volatile material was shown to be $\text{S}_2\text{O}_6\text{F}_2$ by infra-red identification. The material remaining in the tube was shown to be mainly XeF_2 with small amounts of XeF_4 . Analyses gave the following results:

	<u>Expt'l</u>	<u>Theor.</u> (XeF_2)
Xenon %	74.4	77.6
F %	24.05	22.4

This reaction may have involved dissociation of SO_3F_2 into F atoms and $\text{SO}_3\text{F}^\cdot$ radicals. The latter could have combined to form $\text{S}_2\text{O}_6\text{F}_2$ while the former yielded xenon fluorides.

In an attempt to prepare a xenon fluoro-sulfate, 0.0034 mole of XeF_2 was allowed to react with 0.0117 mole of SO_3 at 120°C . After 5 days the reactor was removed from the oven and quenched in water. The tube was further cooled to -78°C and then pumped on through a trap held at liquid nitrogen temperatures. The volatile materials were shown to be xenon and oxygen. The remaining material in the tube was found to be $\text{S}_2\text{O}_5\text{F}_2$ by infra-red identification. Apparently the reaction was $\text{XeF}_2 + \text{SO}_3 = \text{Xe} + \text{S}_2\text{O}_5\text{F}_2 + \frac{1}{2} \text{O}_2$.